

The resistances of the two elements are represented by the following equation:

$$R_{catalytic} = R_o[1 + \alpha(T + \Delta T_{comb})]$$

$$R_{reference} = R_o[1 + \alpha T]$$

with  $R_o$  the resistance at 0° C.,  $\alpha$  the temperature coefficient of resistance,  $T$  the temperature of operation in ° C. and  $\Delta T_{comb}$  the rise in temperature caused by the oxidation of combustible gases on the catalytic layer,  $\Delta T_{comb}$  is given by:

$$\Delta T_{comb} = (R_{catalytic} - R_{reference}) / \Delta R_o = \Delta R / \alpha R_o$$

with  $\Delta T_{comb}/1000$  ppm of combustible gas defined as the sensitivity of the sensor.

FIG. 2 shows a perspective view and FIG. 3 shows a schematic cross-sectional diagram of one of the device configurations fabricated and studied. Two thin-film resistors are fabricated on two micromachined membranes of low thermal conductivity, and one is covered by a catalytic layer. For simplicity, no heater was incorporated in the design and the devices were heated externally.

The average temperature rise in a microcalorimeter is dictated by the balance of heat produced by the chemical reaction and the heat lost to the environment. In order to maximize the detection limit of the sensor, effects such as the reactant mass transfer, the reaction kinetics at the catalyst, the heat loss by conduction/convection to the ambient gas and by conduction to the substrate, thermal fluctuations in the environment, and the electrical characteristics of the thermometer must all be taken into account.

The key elements of a Si-based microcalorimeter are the catalytic layer, the temperature measuring layer, the heater, and the supporting structure or substrate for all of the previous elements. The substrate consists of a bulk silicon frame with either a membrane layer or a more complex plate/teeter element which in both cases are obtained by etching the underlying bulk silicon frame. The membrane or plate/teeter acts as a support for the temperature measuring layer. Multiple silicon dies can be fabricated from a single silicon wafer. The membrane or plate/teeter should have a small thermal mass for fast response time, but must be mechanically robust to support the temperature measuring layer and the catalytic layer and survive temperature cycling, pressure shocks, water mist and small particle impingement. It should also be configured in such a way as to minimize the heat loss to the silicon frame and to the ambient gas for increased sensitivity. The catalytic layer should have a large specific surface area for the device to operate in mass-transport limited regime. This surface area is achieved by using sol-gel processed alumina-silica washcoat and/or sol-gel processed catalytically active metal particles.

Additionally, good thermal contact between the catalytic layer and the underlying temperature measuring layer is also important for increased sensitivity. The catalytic layer should not substantially change the thermal characteristics of the membrane, otherwise the sensor temperature compensation may be compromised. For greater sensitivity, the temperature measuring layer should mainly measure the central region of the membrane where the temperature rise due to the reaction is the largest, without substantially contributing to conductive heat loss. A thin-film resistor with stable resistance and temperature coefficient of resistance (TCR) is desirable as the temperature measuring layer. The film resistor is patterned as a winding element to increase its resistance (i.e., the output signal) and distribute the stress induced by the thermal mismatch with the membrane.

There are three ways to process the sol-gel catalytic layer. One method includes using a micro syringe to deposit the

catalytic layer onto the membrane. With this method, the catalytic layer is deposited to create catalytic active sites specifically at the desired locations. Although this technique provides accurate deposition of the catalytic layer, this technique may not be suitable for mass manufacturing.

A second method involves dipping the silicon wafer into a sol-gel solution to coat the silicon die with a sol-gel processed catalytic layer. This second method is preferred as it provides a controllable and efficient method to batch fabricate catalytic calorimetric gas sensors in a way that is compatible with silicon micromachined structures. The thickness of the catalytic layer can be readily controlled by varying the speed with which the silicon wafer is immersed and removed from the sol-gel solution. This dipping method further requires removal of the sol-gel catalytic layer from specific areas to create the catalytic active sites at the specific desired locations. Selective removal of the catalytic layer can be effectuated in two ways. One involves fabricating a mask on the silicon wafer and placing the mask over the substrate which is then followed by etching away the sol-gel catalytic layer from the undesired locations. The second involves heating the catalytic layer by resistive heating of the membrane on which a catalytic active layer is desired such that the solvents within the sol-gel catalytic layer burn off, resulting in the affixation of the sol-gel catalytic layer in the desired areas. This step is then followed by washing the sol-gel catalytic layer with a solvent to strip the remaining sol-gel solution from the catalytic layer. An acid solvent could strip the solution from the undesired locations. The result in either case is a silicon wafer having a sol-gel processed catalytic layer selectively placed thereon that is easily reproducible. At this time, the preferred method includes dipping the silicon wafer and then etching away the sol-gel solution from the undesired locations.

With the preferred method of fabricating a silicon microcalorimeter, the membrane is deposited first on a silicon wafer, 100 mm in diameter, 400  $\mu$ m thick. The membrane is in total preferably between 500–1000 nm, such that it is mechanically stable while being thin enough to prevent loss of heat by thermal conduction through the substrate. Either a 0.6  $\mu$ m thick layer of low-stress, low pressure chemical vapor deposition (LPCVD) silicon nitride, or a composite of plasma enhanced chemical vapor deposition (PECVD) silicon oxide/nitride layers (about 0.5  $\mu$ m and 0.1  $\mu$ m, respectively) deposited over 0.1  $\mu$ m of LPCVD nitride can be used. After annealing at 600° C., the latter composite layer has a small residual stress (tensile) of about  $6 \times 10^8$  dynes/cm<sup>2</sup>, the compressive state of the oxide being compensated by the tensile nitride. A Pt film resistance thermometer, 100 nm thick, is sputter deposited. The film resistors, acting as temperature measuring devices and/or heaters, are delineated by lithography and wet etching. After annealing the Pt resistors at 500° C. in nitrogen to stabilize their resistance and temperature coefficient of resistance (TCR), the wafers are coated with 0.2–0.3  $\mu$ m of PECVD silicon nitride for passivation and annealed at 500° C. The passivation is then removed on the contact pads with plasma etching. While defining the opening for the contact pads, an etch-mask pattern is also defined on the back side of the wafer using a double-sided aligner. A 30% aqueous solution of KOH at 80° C. is used to completely etch the silicon underneath the membrane. The membrane has sufficient mechanical strength to allow the wafer to be diced with a diamond saw. For ease of handling, a die size of 7×7 mm<sup>2</sup> is used, although only a 3.5×3.5 mm<sup>2</sup> area is needed for the device with the smallest membrane.

While the best mode for carrying out the invention has been described in detail, those familiar with the art to which